https://doi.org/10.26682/sjuod.2023.26.2.58

Journal of University of Duhok., Vol. 26, No.2 (Pure and Engineering Sciences), Pp 650 - 660, 2023
(Special Issue)

BIODIESEL PRODUCTION FROM WASTE COOKING OIL AND ISOPROPANOL FLUID BY USING TRANSESTERIFICATION TECHNOLOGY AND OPTIMIZING THE PROCESS BY USING RESPONSE SURFACE METHOD (RSM)

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(Accepted for Publication: November 27, 2023)

ABSTRACT

Biodiesel represents an important future source of renewable energy, and it consists of waste cooking oil. Waste cooking oil is fatty acid that needs transesterification to produce a methyl or ethyl ester. This research is a study of biodiesel production from two sources, isopropanol and waste cooking oil by using a process of transesterification. The temperature during the experiment was between 300 and 350 °C, the co-solvent(hexane) was between 0 and 8 ml, and the ratio of oil to isopropanol molar ratio was between 4 and 12. According to the findings of optimization studies. The supercritical isopropanol reaction can produce an ideal yield of 91.625% under optimal conditions (the molar ratio of isopropanol to oil is 8.413, the temperature is 326.762 °C, and the solvent is 4.984 ml). The technique was optimized by looking at the biodiesel yields from waste cooking oil and isopropanol under various circumstances. The parameters of the process for the transesterification reaction were optimized using response surface methodology (RSM). The models were effective in explaining the response of the variations regard the three investigated factors. The fuels quality of the produced biodiesel was compared to those required by ASTM for biodiesel.

KEYWORDS: Isopropanol, Trans esterification, Supercritical, Biodiesel, Waste cooking oil.

1. INTRODUCTION

In light of the grave concerns raised by climate change, a large number of industry professionals are currently investigating the possibility of developing and improved a new form of renewable energy source. Because of its properties that help to reduce the greenhouse gases emission. Biodiesel fuel is considered to be the future biofuel that can reduce utilizing the conventional diesel fuel. This is due to the fact that biodiesel fuel has the potential to replace conventional diesel fuel. In comparison to diesel fuel derived from petroleum, biodiesel offers a number of significant advantages. These advantages include a high level of biodegradability and a low level of toxicity. a low level of sulfur and aromatic content [1] and decreased emissions of particulate matter, total hydrocarbons and carbon monoxide (CO) [2]. In addition to, it is comparable to commercial diesel fuel in terms of the cetane number and the produced amount of soot [3, 4]. The vast majority of biodiesel which is produced today is accomplished by a process known as alkali-catalyzed transesterification. Regrettably, throughout the course of the past few years, a wide variety of problems with this approach have been identified. One of the most significant challenges is the necessity, following the reaction, separating the catalyst and the saponified product from free fatty acids. [5] This is one of the challenges. The purifying processes for free fatty acids might make production take more time and create additional complications. The utilization of supercritical technology considered as one of the most promising alternative method for producing biodiesel. The capability of using a wide variety of feedstocks, a faster reaction rate and an easier separation are just some of the many advantages offered by this approach. This technology does not produce an effluent and does not require the use of a catalyst. Several studies conducted to this point have focused on the behavior of reactions [6, 7], the kinetics of reactions [6, 7] and the energy

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analysis of reactions [6, 7] in order to create biodiesel by using supercritical methanol and ethanol (SCM and SCE). In addition, cutting-edge strategies for the production of glycerol-free biodiesel have been subjected to extensive investigation and some of these strategies included the utilization of supercritical methyl acetate, dimethyl carbonate and tert-butyl methyl ether [8]. In another innovative approach to biodiesel production, the pressure inside the reactor was maintained at the same level as the surrounding air while the temperature of the solvent was raised to a level higher than the critical point.

This approach got benefit from non-catalytic superheated methanol technology. In light of the fact that low-carbon alcohols like methanol and ethanol are corrosive, hygroscopic and they have low levels of energy content [9], it is preferred to make use of higher-carbon alcohols like propanol. Both fermentative and petrochemical processes can be used to produce propanol from glucose in a commercial setting. The metabolically modified Escherichia coli and the keto-acid pathway are required for this manufacturing process. In addition to D-glucose, other substances, such as L-rhamnose, glycerol and Dglucose can now be utilized in the synthesis of propanol. Propanol has an advantage over ethanol even in terms of carbon yield in the fermentation process. Due to the fact that propane can be generated from glucose without releasing any CO_2, but the biosynthetic pathway for ethanol contains steps that release CO_2. Hence, the utilization of propanol as a reaction medium in the production of biodiesel has a promising outcome in the future. In contrast to processes that take place in media containing methanol and ethanol, very little study has been done on the synthesis of biodiesel in supercritical propanol (SCP). Only tried to generate biodiesel in a batch reactor using alcohols, including propanol, in supercritical conditions., The maximum temperature which reaction can reach was 300 degrees Celsius. Because of this, the purpose of this study is to determine the conditions under which the greatest amount of biodiesel may be produced, and these criteria involve three different parameters (temperature, oil to isopropanol molar ratio and co-solvent) [2].

2. METHOD AND MATERIAL

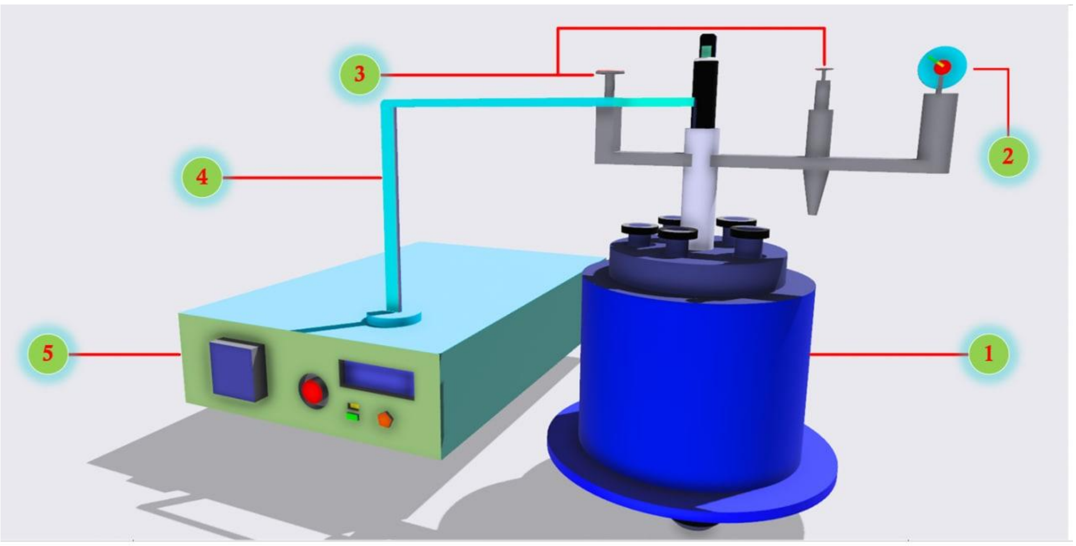
2.1 Material

High purity chemicals were employed in this study without further treatment or purification. The oil collected from various restaurants in Diwaniyah. A supplier of propanol (99%) was used (TEDIA.COMPANY.INC. USA). Well purchased n-hexane (99%) co-solvent from srichem, (new Mumbai. India).

2.2 Experiment

A high-pressure batch reactor with thick walls was used to conduct the reactions. To maintain a steady temperature while the gadget is in use a container with a capacity of 100ml is used. Science Avenue, High-tech District, Zhengzhou, China (as shown in fig. of the experimental setup graph in Figure 1, a control circuit connected to the device to control the temperature, stirrer speed, and time).

To demonstrate the experiment's process According to the calculations specified in the research, the liquid sample (alcohol, oil, and co-solvent) was put in the reactor. To get the reactor to the proper temperature, a heater was used. Since the pressure had to be above the critical pressure in order to establish the reaction time, it was computed using a pressure gauge. The resultant combination of biodiesel and glycerin was removed when the reaction had stopped. The separator used the difference in density to separate the glycerin from the diesel fuel. Diesel fuel was eventually acquired.



Fig(1):- Schematic of Experimental Setup where 1. Electrical Heater, 2. Presser Gauge, 3. Safety valve, 4. Thermocouple, 5. controller

2.3ANALYTICAL METHODS

The liquid product components are examined using a GC-MS (Agilent 6890N series GC with a 5973 N Inert MS detector and 7683 Injector). The GC-MS approach entails a number of steps, including sample preparation, internal standard selection and the generation and analysis of experimental data using GC-MS software's analytical method. Each stage of technique development is evaluated by experimental design, testing, and evaluation. To establish a data analysis procedure in the GC-MS software and interpret experimental results, for instance, changes in sample concentration, selection, and internal standard concentration are created in the sample preparation stage alone. The evaluation of each stage of technique development using an experimental design.

3. EXPERIMENTAL DESIGN

Response surface approach uses mathematical and statistical tools to determine a regression model equation that connects an objective function with its independent variables (RSM). This study examined how process factors affected yield using a 3-level 3-factor Box-Behnken design (BBD). Yield was a reaction to temperature, co-solvent, and isopropanol-to-oil ratio. Process factors were coded using low, middle, and high levels. Table 2 displays the experiment array suggested by BBD for the current work and obtained by Design expert-11 program. Table 1 shows the process parameters with their specified levels.

Table (1):- Process factors and their impact on biodiesel yield

Name	Code	Low (-1)	Middle (0)	High (+1)
Isopropanol to oil	A	4	8	12
Temperature	B	300	325	350
Co-solvent	C	0	4	8

Table (2):- Box- Behnken experimental design

Run	Isopropanol to oil - A	Temperature. B	Co-solvent C
1	8	300	0
2	8	325	4
3	8	350	8
4	4	300	4
5	8	325	4
6	12	325	0
7	12	350	4
8	4	325	0
9	8	350	0
10	4	350	4
11	8	300	8
12	4	325	8
13	12	325	8
14	12	300	4
15	8	325	4

The correlation between the answer and their independent variables was investigated in this study by employing the second-order model listed below, which was solved for using the least-squares approach [10]:

$$Y = a_0 + \sum a_0 x_i + \sum a_{ii} x_i 2 + \sum a_{ij} x_i x_j \qquad (1)$$

Where Y stands for the output (Yield), i and j for the pattern index numbers, a_0 for the intercept term, and x_1, x_2,..., x_k for the process variables in coded form. The letters a_i, a_{ii}, and a_{ij} stand for the first order (linear) main effect, the second-order main effect, and the interaction effect, respectively. After completing the analysis of variance, the model's appropriateness was verified by estimating the regression coefficient (R^2).

4. RESULTS AND DISCUSSION

4.1 Results of Experimental Design

15 runs were carried out in accordance with BBD design to look into the ideal circumstances for biodiesel production. The experimental findings involving actual Yield and predicted Yield are shown in Table 3.

Table (3):- Experimental results of Box–Behnken design for production biodiesel

Run	isopropanol to oil - A	temperature B	Co-solvent C	Actual Value	Predicted Value
1	8	300	0	65	65.25
2	8	325	4	92	91
3	8	350	8	77	76.75
4	4	300	4	70	70.5
5	8	325	4	91	91
6	12	325	0	72	72.25
7	12	350	4	75	75.5
8	4	325	0	73	73.25
9	8	350	0	67	67.25
10	4	350	4	76	76.5
11	8	300	8	72	71.75
12	4	325	8	79	78.75
13	12	325	8	83	82.75
14	12	300	4	75	74.5
15	8	325	4	90	91

Findings indicated that biodiesel production efficiency was in the region of (65- 92). The results of the ANOVA can be used to determine the precise impact of various parameters.

The production biodiesel results were examined using design Expert-11 software, and the following quadratic model of the production biodiesel in terms of real units of process parameters was developed.:

$$Yield = 9 + 0.875A + 1.62B + 4.25C - 1.5AB + 1.25AC + 0.75BC - 5.25A^2 - 11.75B^2 - 9.00\,C^2 \qquad (2)$$

Where AB, AC, and BC are the three-way interactions of the model's parameters. The sum of (A)2 and (B) gives a good indication of the significance of changes to the model's parameters (C). Forecasts of Yield values were made using Equation 2, and the results are tabulated in Table 3. The efficacy of BBD was assessed using analysis of variance (ANOVA). Fisher's F-test and the P-test provide a useful analytical framework for assessing the importance of the model and its parameters. Increased F-values and decreased p-values imply more significant coefficient terms. Table 4 displays the results of the analysis of variance for the response surface model. The model and parameter degrees of freedom are denoted by DF, and the statistical terms sum and adjusted mean by Seq. SS and Adj. MS, respectively, in this table. The regression model was determined to be highly significant, with a p-value of (0.0001) and an F-value of (245.8). As can be seen in Figure 2, the projected and experimental values compare favorably to the existing operating data, as indicated by the line with the unit slope. The multiple correlation coefficient of the model, which was 0.9977, indicates that the regression is statistically significant, since only (0.0032) of the total variations are not supported by the model. In this model, the multiple correlation coefficients are well matched because the difference between the adjusted multiple correlation coefficient (adj. R^2) and the projected multiple correlation coefficient (pred. R^2) is less than 0.1.

Table (4):-Study of variance for biodiesel production

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	995.48	9	110.61	245.8	< 0.0001
A-isopropanol to oil	6.12	1	6.12	13.61	0.0142
B-temperature	21.12	1	21.12	46.94	0.001
C-Co-solvent	144.5	1	144.5	321.11	< 0.0001
AB	9	1	9	20	0.0066
AC	6.25	1	6.25	13.89	0.0136
BC	2.25	1	2.25	5	0.0756
A^2	101.77	1	101.77	226.15	< 0.0001
B^2	509.77	1	509.77	1132.82	< 0.0001
C^2	299.08	1	299.08	664.62	< 0.0001
Residual	2.25	5	0.45		
Lack of Fit	0.25	3	0.0833	0.0833	0.963
Pure Error	2	2	1		
Cor Total	997.73	14			
	R^2	Adjusted R^2	Predicted R^2	Std. Dev.	PRESS
	0.9977	0.9937	0.9915	0.6708	8.5

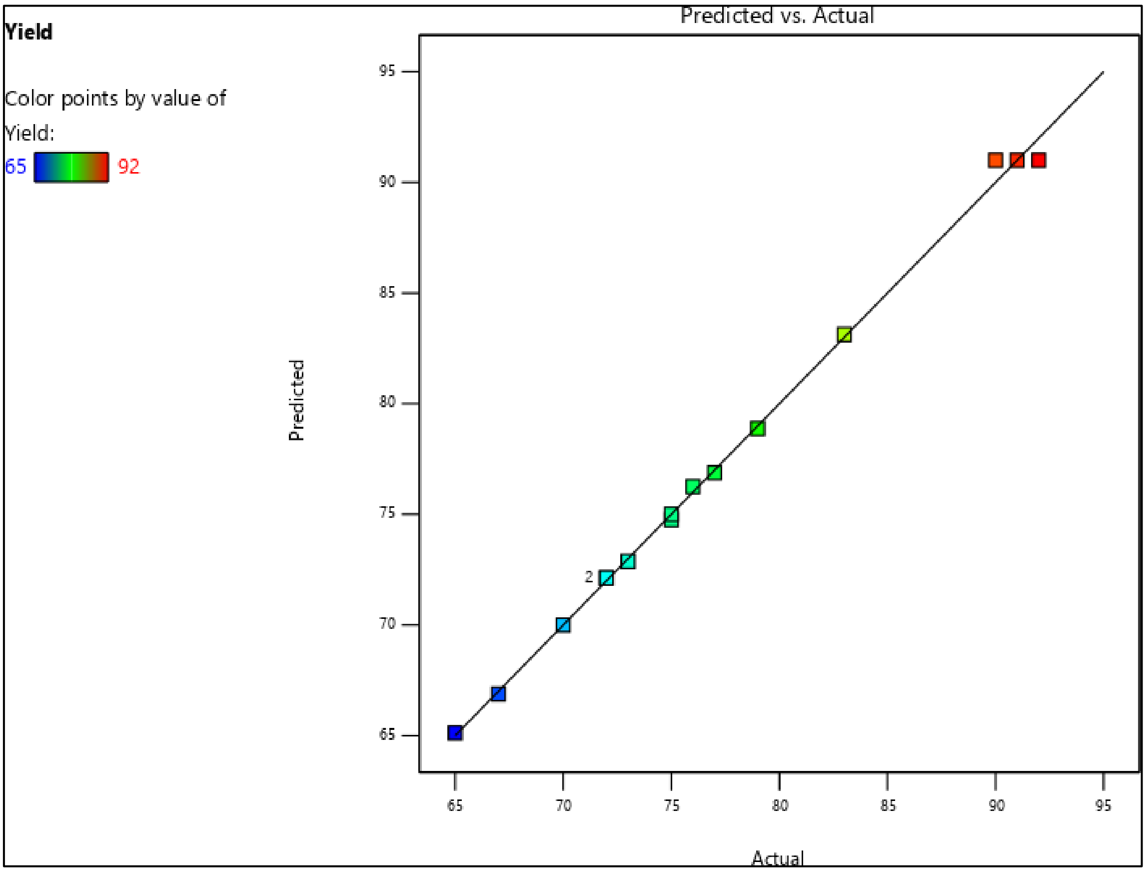
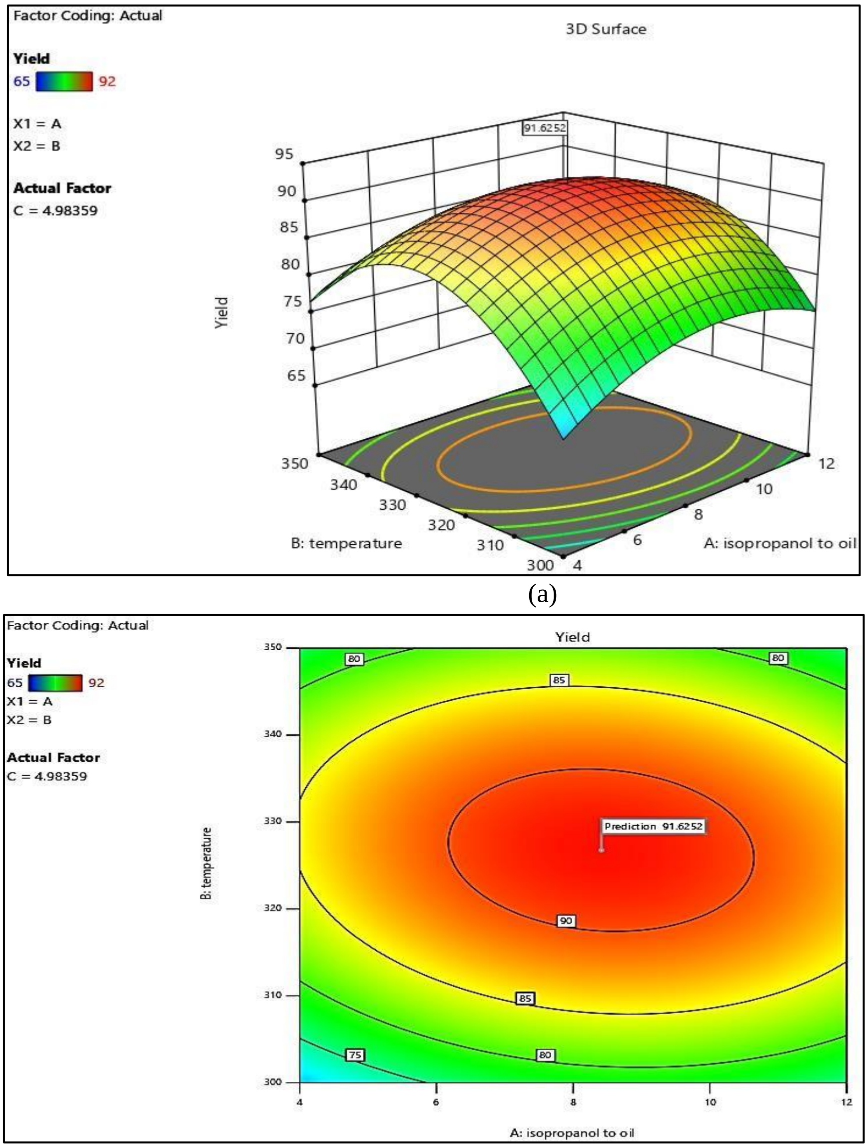


Fig.(2):-Yield biodiesel experimental data versus expected data

The interactive effects of the chosen factors and their impact on the response can be shown graphically using RSM. Figures 3a, b illustrate how the Yield for different ratios of isopropanol to oil (4–12) at constant co-solvent changes with temperature (4.98359). Figure 3-b depicts the corresponding contour plot, while Figure 3a illustrates the response surface plot. The control plot's form reveals the type and degree of the interaction. It was noted from the surface plot that, at isopropanol to oil (4), an increase in Yield occurs as the temperature increases from 300-350. At any temperature, Yield increases linearly with increasing of isopropanol to oil 4 to 12.

According to the stoichiometry of transesterification reaction, three moles of alcohol and one mole of triglyceride is required in order to produce three moles of biodiesel and one mole glycerol. Here, more isopropanol to drive the reaction toward more production of biodiesel was required. So, the increase of biodiesel efficiency may be due to increased contact between the alcohol and oil. Moreover, increasing the isopropanol as reactant can increase the reaction rate [11] .

The related contour figure shows that the Yield value of 92% is within a narrow range where the isopropanol to oil ratio was (6.2–10.3) and the temperature was in the range of (317-335).



(a)

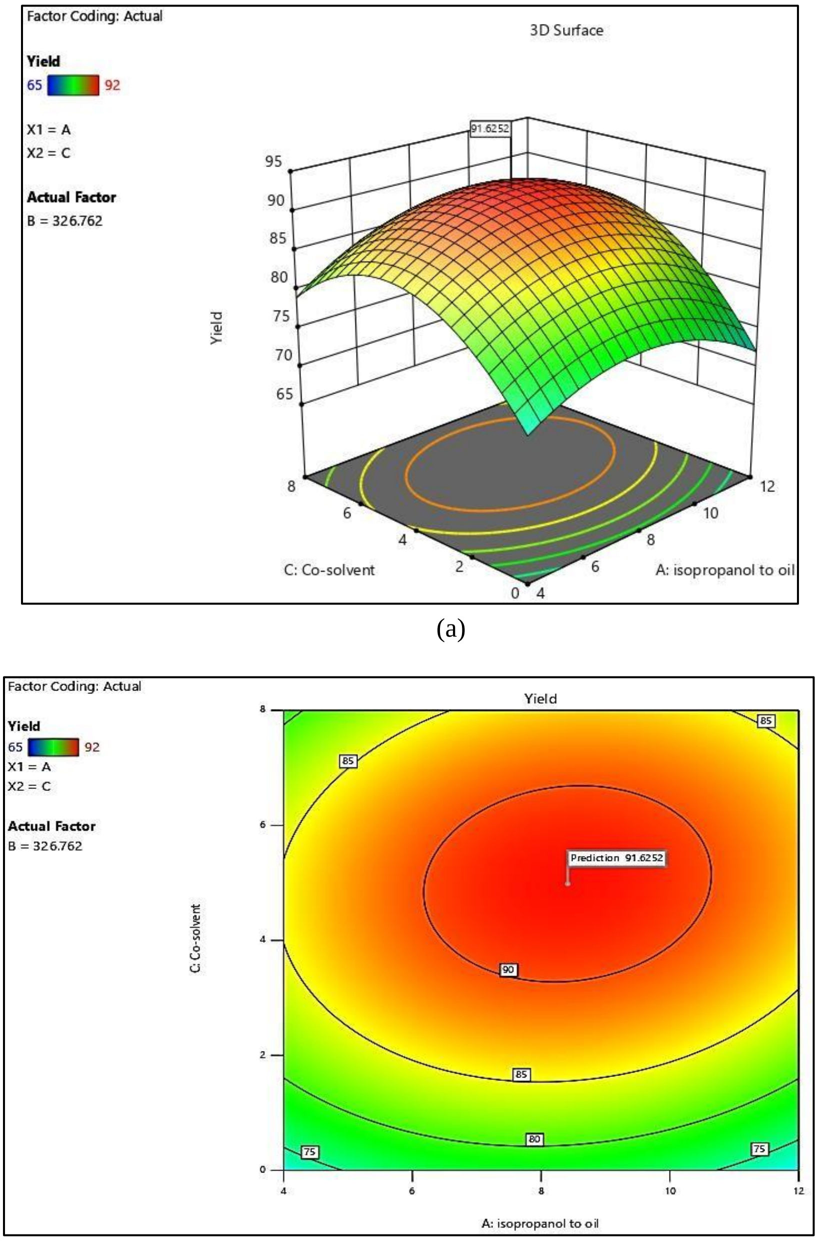
(b)

Fig.(3):-. Response surface plots (a) and contour plots (b) showing how temperature and the ratio of isopropanol to oil affect yield.

The influence of the co-solvent on the Yield for different ratios of isopropanol to oil (4-12) at constant temperature is shown in Figures 4a, b (326.762). The response surface plot is shown in Figure 4a, and the matching contour plot is shown in Figure 4b. The size and type of the interaction are shown by the control plot's shape. It was noted from the surface plot that, at isopropanol to oil (4), an increase in Yield occurs as the co-solvent increases from 0-8. At any co-solvent, Yield increases linearly with increasing of isopropanol to oil 4 to 12.

In this study, as it is clear from equation (2), the presence of additional n-hexane as a co-solvent had a negative impact on the efficiency of biodiesel production. This result contrasts with the results of some articles but is very interesting and meaningful[12]; it can be hypothesized that the presence of Hexane as a Co-solvent cannot be beneficial in all situations. Abedini et al.

The related contour map shows that the Yield value of 92% is within a narrow range where the isopropanol to oil ratio was (6.2–10.2) and the co-solvent ranged from (3.7-6.3).



(a)

(b)

Fig.(4):- Impact of co-solvent and isopropanol to oil on the Yield as represented by the response surface plot (a) and contour plot (b).

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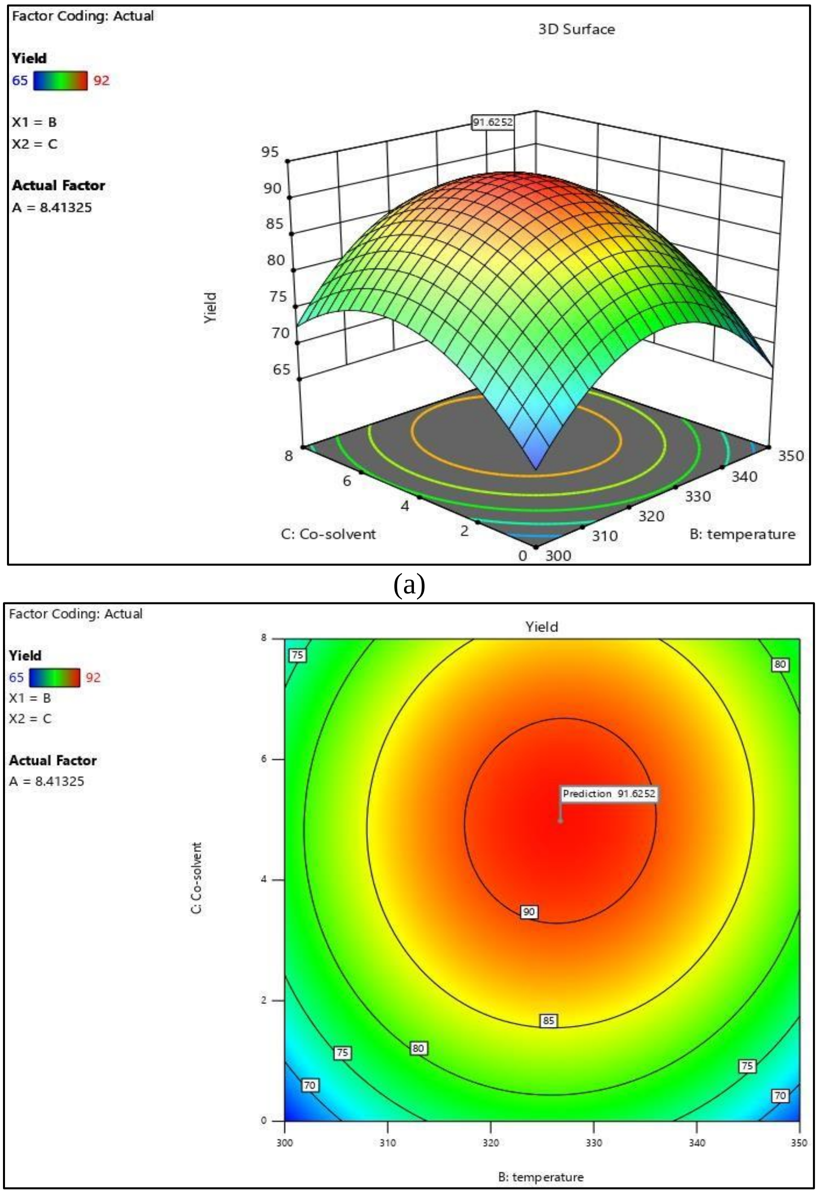
Figures 5a, and Figure 5b demonstrate how the co-solvent on the Yield for various values of temperature (300-350) at constant isopropanol to oil 8.41325. Figure 5a represents the response surface plot while Figure 5b shows the associated contour plot. The shape of control plot indicates the nature and extent of the interaction. From the surface plot, it was observed that, at temperature (300), an increase in Yield occurs as the co-solvent increases from (0-8). At any co-solvent, Yield increases linearly with increasing of temperature 315 to 330 °C

The temperature effect has been presented in many researches and it can be seen, that increasing temperature, due to the endothermic reaction, let the reaction equilibrium to produce more biodiesel. In addition, raising the Temperature will increase the reaction rate, which consequently results in further conversion. It also helps the homogeneity of mixture of oil and alcohol[13].

The associated contour diagram verifies that the value of the Yield 92% lies in a small area in which the temperature ranged between (315-330) and co-solvent in the range of (2.7-6.4).



(a)

(b)

Fig.(5):- The effect of temperature and co-solvent on yield is depicted by a response surface plot (a) and a contour plot (b).

4.2 The Optimization and Confirmation Test

Many criteria should be recognized during system optimization in order to maximize the desirability function (DF) and achieve the intended target [14]. Target functions that are being evaluated include maximize, objective, minimize, within the range, and none. When DF=1.0, the Yield objective was referred to as the "maximum." The co-solvent at range of the process parameters investigated in the present work were (0-8), temperature at range of (300-350), and isopropanol to oil at range of (4-12). yield of 65was taken as lower limit value of the production biodiesel, while 92 was designated as the upper maximum value. Under these boundaries and settings, optimization was carried out and the results are shown in Table 5.

Table(5.):- Optimum of process parameters for maximum Yield.

Response	Goal	Lower	Target	Upper
Yield	maximum	65	Maximum	92
parameters	A: isopropanol to oil	B: temperature	C: Co-solvent	Yield
Optimum parameters	8.413	326.762	4.984	91.625

5. CONCLUSION

In this study, supercritical transesterification processes involving oil were analyzed with response surface methodology (RSM), and the influence of alcohol on those reactions was investigated in great detail. A rate of mixing of 600 revolutions per minute (rpm) and a reaction time of fifty minutes (min) were also implemented. According to the data, it was possible to convert a significant amount of oil into biodiesel at a temperature of 326.762 degrees Celsius, a molar ratio of 8.413, and a co-solvent of 4.984, I, with a maximum biodiesel production of 91.625 %. This model has a p-value that is more than 0.0001 and an R2 value that is equal to 0.9977. The response surface method was utilized in order to study the transesterification process that occurs during the production of biodiesel from sunflower oil (RSM). The fact that the models and the results of the experiments agreed well demonstrates that the methodology in question is beneficial to the process of optimization.

Acknowledgment

The team would like to thank the faculty and students of the Chemical Engineering department at University of Al- Qadisiyah for their contributions to this study.

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